PERMEABILITIES OF COLLOIDAL SUBSTANCES TO GASES.

By **Kazuo KANATA.**

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It is a well known fact that almost all amorphous substances, especially colloidal substances, absorb various gases, but the mechanism is not yet clear. The India rubber, for example, is permeable to various gases[1]. In the present experiment it has been examined whether other colloidal substances are also permeable for gases or not, and hence whether their sorption is an adsorption phenomenon or not. The author wishes, also, to discuss on the mechanism of the permeability and absorption.

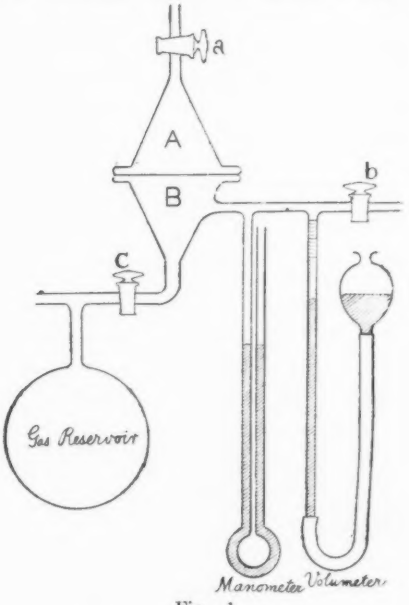

Fig. 1.

Experimentals. The apparatus used in this experiment is shown in Fig. 1. The membrane of the colloidal substance to be examined is placed between A and B. The stop-cocks a and b are opened and the air exist in the vessel and some gases which may be sorped in the mass of the membrane are exhausted by a pump. Then the cocks a and b are closed, and the gas under examination is introduced into B through the cock c. The volume change of the gas is measured with a volumeter.

The membranes used were of rubber, celluloid and gelatine, while the gas tested were hydrogen, oxygen, carbon dioxide, sulphur dioxide and ammonia. For the first several hours, before the stationary state is reached, the effect of absorption is very large. The data shown in the following tables were obtained.

(1) Graham, *J. Chem. Soc.*, **20** (1867), 235; Wroblewski, *Ann. Physik*, **8** (1879), 29; Hüfner, *Ann. Phys. u. Chem.*, **34** (1886), 1; Edwards and Pickering, *Chem. Met. Eng.*, **23** (1920), 17; Daynes, *Proc. Roy. Soc.* (*London*), **97** A (1920), 286; Venable and Fuwa, *Ind. Eng. Chem.*, **14** (1922), 139.

TABLE 1.

Celluloid.

Oxygen		Hydrogen		Carbon dioxide		Ammonia	
Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.
5	0.32	10	0.40	9	1.14	8	9.46
10	0.48	20	0.72	19	1.90	16	16.45
20	0.68	30	0.92	29	2.52	26	22.80
30	0.80	40	1.26	59	3.72	38	28.25
50	1.20	60	1.72	99	5.18	44	36.97
81	1.34	90	2.39	119	5.64	65	41.37
120	1.67	120	3.10	149	6.57	90	47.62
180	1.97	180	4.36	179	7.43	120	57.61
251	2.40	240	5.74	239	9.24	150	69.07
307	2.47	300	7.18	310	11.37	180	75.10
371	2.70	365	8.40	370	13.11	233	92.00
428	2.86	420	9.57	430	14.80	290	104.91
480	3.06					345	115.37
						413	129.34

These data are depicted in Fig. 2.

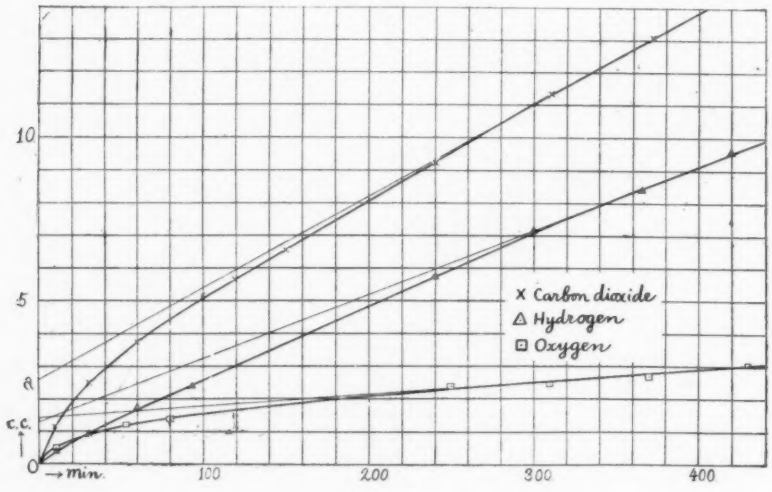

Fig. 2.

TABLE 2.

Rubber.

Oxygen		Hydrogen		Carbon dioxide		Sulphur dioxide		Ammonia	
Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.
10	0.04	5	0.133	5	0.58	13	18.57	8	10.83
20	0.05	10	0.185	10	0.86	22	26.50	17	19.46
50	0.17	20	0.230	20	1.357	32	33.59	28	27.32
110	0.33	30	0.285	31	1.76	42	37.78	40	35.59
240	0.78	40	0.385	40	2.16	50	43.40	48	40.02
300	0.91	50	0.44	50	2.49	60	47.36	58	45.77
367	0.99	60	0.472	60	2.80	90	57.63	90	61.54
436	1.08	90	0.617	90	3.57	120	65.56	150	88.36
1372	2.95	120	0.887	120	4.29	180	78.03	200	106.34
		180	1.219	180	5.66	240	88.43	310	137.50
		240	1.503	240	6.633	300	97.00	410	165.43
		300	1.875	300	7.954	360	105.97	530	192.34
				423	10.23	422	114.45		

(The measurements on the ammonia and the sulphur dioxide have been suspended after the time shown in the bottom line of the table until the stationary state was reached.)

TABLE 3.

Gelatine.

Oxygen		Carbon dioxide		Sulphur dioxide.	
Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.
5	0.06	5	0.058	10	0.55
10	0.11	10	0.162	20	1.09
21	0.16	20	0.235	30	1.35
30	0.19	30	0.254	40	1.62
40	0.22	60	0.402	50	1.90
50	0.30	120	0.556	55	1.98
60	0.36	180	0.664	85	2.58
133	0.43	240	0.78	175	3.68
421	0.64	360	0.79	235	4.28
1375	0.815	450	0.85	295	4.82
		1410	1.328	355	5.24
				445	5.82

(The measurement on the ammonia was done only after the stationary state was reached.)

We must, therefore, continue the experiment until the volume change becomes constant, and then determine the permeability by dividing the volume change by the time interval. The relative permeabilities to the various gases are shown in the following table. (in the case of rubber, permeability to hydrogen has been taken as unity; but in other cases, oxygen as unity.)

TABLE 4.

Membrane / Gas	Celluloid	Rubber	Gelatine	Viscosity coeff. of gas at 20°C.	Square root of gas density
Hydrogen	2.60	1.00	less than 1.00	930×10^{-7}	1.41
Oxygen	1.00	0.35	1.00	2120×10^{-7}	5.66
Carbon dioxide	8.76	3.17	4.13	1600×10^{-7}	6.63
Sulphur dioxide	—	7.90	31.90	1380×10^{-7}	8.00
Ammonia	62.3	11.4	95.2	1080×10^{-7}	4.12

Theoretical Considerations. As it became clear that these substances are permeable to gases, there is no doubt that the sorption of various colloidal substances is not an adsorption phenomenon, that is condensation of the gaseous molecules on the surface of the substance only. It will, then, be discussed something about the mechanism of the absorption judging from the present experiments. For the passability of the gas through the membrane two causes can be considered, namely the passing of gas through the pores of the substance and the dissolution.

Pass through the Pores of the Membrane. As for the porosity of the colloidal substance many authors have discussed for long time. If we assume the permeability is due to the porosity, we have to consider two cases, namely, the viscosity flow and the molecular flow.

In the case of the viscosity flow, the rate of permeabilities for various gases will be inversely proportional to the viscosities of gases, as shown in the following well known equation.

$$q = \frac{\pi r^4 (p_0 - p)\, t}{8\eta\, l}$$

where q denotes the mass of the gas which pass through the unit area of the membrane and η, the viscosity coefficient of the gas. The viscosity coefficients of the gases are shown in the 5th column of Table 4.[1] Thus ammonia is more viscous than hydrogen, while the former is far more passable through membranes than the latter. It is known, therefore, that the viscosity flow is not the main cause of the permeability.

(1) Landolt-Börnstein, "Physikalisch-chemische Tabellen", 5 ed.

If the radius of pores is very small and the mean free path of the molecules is not negligible compared with the radius of pores it is the case of the molecular flow, and the permeability is inversely proportional to the square root of the density of gas.(1) But such a relation does not exist as shown in Table 4.

Dissolution. As has been discussed above, it is not quite plausible to assume that the permeability is due to the porosity. I think it is due to the solubilities of the gases into the membranes, and this idea is supported by many other facts. For example, the order of the solubilities of gases in these substances are almost the same as those in other substances like water. The gases of lower polarity is dissolved less while those of higher dissolved much. By the aid of the Fick's law the dissolution theory can also explain the fact that the orders of permeabilities are inverse to those of absorption in some cases.

From the Fick's law,

$$\frac{dq}{dt} = -D\frac{dy}{dx}$$

where y denotes the concentration at x, we have the following equation by using the Fourier's expansion,

$$y = y_1 + (y_2 - y_1)\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{n=\infty}\frac{y_2\cos n\pi - y_1}{n}\sin\frac{n\pi}{l}x.\, e^{-Dn^2\pi^2 t/l^2}$$

In the present experiment,

$$y_1 = 0 \quad at \quad x = 0.$$

By the Henry's law we have the following condition,

$$y_2 = Ap \quad at \quad x = l$$

where A is the absorption coefficient.
We obtain, therefore,

$$q = \frac{DAp}{l}\left[t + 2\sum_{n=1}^{n=\infty}\frac{l^2}{Dn^2\pi^2}(1 - e^{-Dn^2\pi^2 t/l^2})\right]$$

and when t is large this equation takes the form,

$$q = \frac{DAp}{l}\left(t + \frac{l^2}{3D}\right)$$

In this equation the first term $DApt/l$ is the quantity of the gas which passes through the membrane after the stationary state has been reached. From this it can be understood that the permeability is related to both the

(1) Loeb, "Kinetic theory of gases", p. 252.

absorption coefficient (A) and the diffusion coefficient (D). Therefore, if D is very large or very small compared with A, the orders of the permeabilities are not the same as those of the absorption. The second term $Ap\,l/3$ corresponds to Oa in Fig. 2.

From the present experiments it cannot be judged whether the dissolution is a purely physical phenomenon or the chemical changes occur at the same time. But, in the case of the rubber it has been shown by Edwards and Pickering[1] that the solubility of sulphur dioxide is greater than that of ammonia. On the contrary, in the ordinary solvent, the solubility of ammonia is greater than that of sulphur dioxide. It is probable that there occurs some chemical change in this case. In the case of ammonia through celluloid, after putting the membrane in the atmosphere of ammonia for a long time, the permeability increased as much as five times in comparison with the data shown in Table 4—0.2056 c.c. per min. in the experiment from which Table 4 was obtained, while 1.110 c.c. per min. after putting it in the atmosphere of ammonia for about four days—and the colour changed from white to yellow and increased transparency. Such effects also might be due to the chemical change. I think that it may be due to the chemical change in the most cases where the ammonia is dissolved much in solvent.

Summary.

1. Permeabilities of rubber, gelatine and celluloid for oxygen, hydrogen, carbon dioxide, sulphur dioxide, and ammonia were determined.

2. By ascertaining the permeabilities of celluloid and gelatine, it became clear that the sorptions of these substances are not adsorption phenomena.

3. Something about the mechanism of permeability and absorption was discussed and the author reached the conclusion that the permeability and hence the absorption is caused by the dissolution of gas in the colloidal substance.

In conclusion I wish to express my sincere thanks to Prof. J. Sameshima for his kind guidance during this experiment.

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(1) Loc. cit.

THE EFFECT OF GELATINE ON THE POLYMORPHIC TRANSFORMATION OF MERCURIC IODIDE.

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The author studied the effect of various colloidal substances on the formation of mercuric iodide from mercuric chloride and potassium iodide solutions.[1] In the present note the effects of gelatine on the transition between red and yellow modifications of mercuric iodide are described.

The mercuric iodide was prepared from the equivalent quantities of the solutions of mercuric chloride and potassium iodide, and then it was washed with water and dried. About 0.5 gram of gelatine was dissolved in a few cubic centimetre of hot water and added about 20 grams of mercuric iodide, mixed them well by grinding in a mortar. The viscid red mass thus produced was spread on a glass plate, which had previously been coated with a thin film of paraffin in order to prevent the sticking of gelatine on the surface of glass when dried. After the mass was dried, it was taken off the glass plate, and a few of the small pieces was put in a glass capillary tube.

The pure mercuric iodide powder was put in a capillary tube of the same dimensions as above. These two tubes, the one containing the gelatinized mass and the other the pure mercuric iodide, were put in a bath of the heating liquid ("liquid paraffin" was used) side by side providing a thermometer and a stirrer. Then the liquid was heated and the colour changes of the two tubes were observed.

The heating rate was about one degree per five minutes. At 125–130°C. the colour of the pure mercuric iodide began to turn yellowish, and at 132°C. it changed to yellow completely. The gelatinized mercuric iodide, however, showed no sign of colour change at this temperature and remained in red. The gelatinized one began to change its colour at about 150°C. and it turned more and more yellowish by the elevation of the temperature. At so high a temperature as 168°C. the colours of the two capillary tubes became identical.

Now the burner was turned off and the bath was left to cool. At a temperature lower than 127°C. there appeared some red spots in the pure mercuric iodide tube, and increased their areas by and by, which at last, after a few minutes, spreaded all over the mass of iodide and turned completely to red form. Yet, the gelatinized one retains its yellow colour

(1) Sameshima and Suzuki, this journal, **1** (1926), 81.

even after cooled down to the ordinary room temperature. After some times, the surface of the gelatinized yellow mass is contaminated with some red powder, which is small crystals of mercuric iodide sublimed out onto the surface from the gelatinized mass. Therefore, if the mass is taken out from the tube and broken, it can be seen that the inside of it is quite yellow. The inside of the gelatinized mass remains yellow for months after the time of heating. Thus the yellow form may remain unchange at ordinary tempera ture for indefinite length of time. But if we scratch the yellow part with something like a pencil knife the part immediately turns to red.

The above described phenomena may be interpreted as follows. In the present case, gelatine act as a protecting colloid in solid phase. It retards the velocities of transformations between red and yellow mercuric iodide, over and under their transition temperature 127°C. It is a general fact that, in a mean time, there may take appearance a few number of nuclei of the stable phase out of the supercooled or superheated phase. These nuclei, then, grow in their size and at last all of the mass changes to the stable phase. But if there exist the gelatine or other colloidal substances and each particles of the supercooled or superheated phase are enveloped by these colloid, then the growing of the nuclei will be hindered, even though they appeared here and there. We may say, in general, that the transition point between enantiotropic modifications will be made unsharp by the presence of the colloidal impurities, or shows hysteresis in the transition temperature. In the other hand, these phenomena may throw some light on the Smits' theory of allotropic modifications.

An interesting lecture demonstration can be performed in the following manner. One gram of gelatine is dissolved in 10 c.c. of hot water, and the solution is transferred into a mortar, add 20 grams of mercuric iodide and mix thoroughly by grinding with a pestle. The red viscid mass thus obtained is then spread by a brush on a clean glass plate to a thin layer, and dried by gently warming on a water bath. Now half a gram of gelatine is dissolved in 5 c.c. of hot water and paint it over the red coating above described. The latter treatment is necessary because it prevent the deposition of the sublimed mercuric iodide crystals on the surface of the gelatinized layer. After drying, the plate is put in an air bath and uniformly heated to about 170° C. in a draught chamber. When the plate turns to yellow completely, it is taken out from the bath and left to cool.

The yellow plate thus obtained will retains its colour for indefinite length of time. It is the protected supercooled yellow modification of mercuric iodide. Now the plate is brought before the audience, and scratch the yellow mass with the finger nail or a pencil knife. The scratched portion will immediately changes its colour to red, while the untouched

portion will remain in yellow. We can write, therefore, some letters or figures in red colour on the yellow surface.

Moreover, an interesting fact was observed. On heating the gelatinized red iodide on a desk near the window, the lighter side of the mass turns yellow first and then the darker side follows it afterward. On keeping the yellow mass near a window at the ordinary temperature, the light side of the surface contaminated firstly with the red powder of sublimed iodide, while the dark side remains yellow longer. Thus the light energy accelerate the transformation velocity of the polymorphic changes.

Summary.

The mercuric iodide containing gelatine shows hysteresis on the transition temperature, i.e. it is necessary to heat considerably higher than 127°C. to transform the red modification into the yellow one, and on the contrary, the yellow one remains unchange for indefinite length of time at the room temperature. In this case gelatine act as a protecting colloid in a solid phase.

A lecture demonstration has been described of showing the behavior of the protected suppercooled mercuric iodide. See errata V. 2, P. 321

The transformation of mercuric iodide of metastable form to that of stable one is accelerated by the light energy.

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MICRO-IDENTIFICATION OF ISOMERS AND HOMOLOGUES IN THEIR MIXTURE. I. THREE ISOMERIC XYLENES.[1]

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Xylene occurs more or less in almost every sample of petroleum. In coal-tar it is one of the chief constituents of the "solvent naphtha", and it is contained also in raw wood-spirit. Thus xylene is very often met with in

(1) More detailed description shall be given in the Nippon Kwagaku Kwaishi in Japanese.

studies of hydrocarbons, yet satisfactory methods to identify its three isomers, *o*-, *m*- and *p*-xylenes, especially in a sample of limited quantity, could not be found in literature.

It would be proper to consider that xylene, obtained by dry distillation of natural products, is a decomposition product of more complicated substances. If we can ascertain to which of three isomers the xylene in question belongs, it would enable us to get a key to trace its origin in the mother substances. For this purpose, I have tried to detect and identify three isomeric xylenes in their mixture with the smallest quantity of the sample. Two methods, sensitive colour-reaction and observation under microscope, were tried for identification in micro-scale.

I. Colour-reaction.

Among phenomena such as oxidation, reduction, halochromy, pseudomerism, etc., which produce colour-change, pseudomerism seems to have the widest application in analytical field. Nitro-compounds often give sharp colour-reactions when they are transformed from nitro- to aci-form; detection of primary and secondary alcohols by V. Meyer's method and Liebermann's reaction for secondary amines are good examples of application of pseudomerism of nitro-derivatives.

On the colour-reactions of nitro-derivatives of aromatic hydrocarbons, Stultz[1] describes that alcoholic solution of trinitro-pseudo-cumene gives with a drop of caustic potash an intense green coloration which turns brown after a short time. Trinitro-*m*-xylene gives under the same condition similar colour-reaction, while 2, 4-dinitro-toluene produces a pure blue colour and 2, 4, 6-trinitro-toluene a fuchsine red. On the other hand, no colour change is observed in the case of 2, 6-dinitro-toluene and trinitro-mesitylene.

Lepsius[2] describes also that 2, 4, 6-trinitro-toluene gives in acetone solution a bordeaux red coloration.

As no description is found about trinitro-*p*-xylene, I have prepared from pure *m*- and *p*-xylenes their trinitro-derivatives (2, 4, 6-trinitro-*m*-xylene and 2, 3, 5-trinitro-*p*-xylene), and examined their colour-reactions towards alkali in some solvents.[3]

(1) *Ber.*, **42** (1909), 3608.
(2) *Chem. Zt.*, **20** (1896), 839.
(3) As for *o*-xylene, it is known for its stability toward nitrating agent, and under the same condition in which *m*- and *p*-xylenes form trinitro-derivatives, it only forms oily lower nitro-compounds.

1. **Alcoholic solution.** With a drop of caustic potash, the *m*-compound in this solution gives instantly an intense bluish green coloration which turns on standing dull yellow, and finally a dark brown precipitate settles from the solution. In the case of the *p*-compound colour does not develop instantly, but in a few second the solution is tinged orange and then turns to a reddish brown tone, similar to that of iodine-tincture. On standing, the solution becomes turbid and a reddish brown deposit appears.

Thus we can observe remarkable differences in the two colour-reactions: (1) The colours produced by the two components form a fair contrast. (2) Both colorations do not occur simultaneously; one takes place instantly, while the other after a sufficient interval. (3) In the first the coloration fades in its tone while in the second it becomes deeper in the course of time.

From these facts we can expect that these reactions may be highly sensitive when applied to the detection of *m*- and *p*-xylenes in their mixture. In fact, when a mixture of the two alcoholic solutions above mentioned is treated with a drop of alkali, bluish green coloration appears at once, and after a short time, the reddish colour, characteristic to trinitro-*p*-xylene, predominates. The tinge of the first coloration and the time required for appearance of the second, are variable with different proportions of the two components. The larger the quantity of the *m*-compound is, the more intense is the green coloration and the longer is the time required. For example, light green colour, which is immediately followed by the second coloration, is distinctly observed with a mixture of 2 c.c. of alcoholic solution of the *p*-compound and 0.05 c.c. of that of the *m*-compound. According to Blanksma[1] 100 c.c. alcohol dissolves 0.039 gr. trinitro-*m*-xylene at 20°C., consequently only 0.00002 gr. of the *m*-compound is contained in 0.05 c.c. of the alcoholic solution. The above example serves to show the sensitivity of this colour-reaction.

2. **Acetone solution.** The colours produced by the trinitro-*m*- and *p*-xylenes in this solution, with a drop of caustic alkali, are dark green and reddish brown respectively, and both colorations take place instantly, and do not change rapidly in their tones. Therefore, in case of mixture, a mixed colour is observed. For example, an acetone solution containing two trinitro-compounds in about equal proportion, takes a violet hue. On the other hand, in a mixture very rich in one of the components, the colour produced by the other can hardly be distinguished. Therefore, this reaction

(1) *Rec. trav. chim.*, **25** (1906), 177.

appears, at first sight, to be of no value for analytical purpose. Nevertheless, this colour-reaction is indispensable to detect and identify the very small quantity of *p*-xylene in a mixture rich in *m*-xylene; for acetone dissolves, even when hot, only a trace of trinitro-*m*-xylene but readily the *p*-compound. On the other hand, as the two nitro-compounds are almost equally soluble in alcohol, if the identification of the same sample is carried out in alcoholic solution, the colour produced by the *p*-compound will be ambiguous.

In conclusion, in the case of a mixture of pure isomeric xylenes we can successfully detect and identify *m*- and *p*-xylenes by colour-reactions of their trinitro-compounds either in alcoholic or in acetone solution.(1) But in the case of a mixture with other compounds, as is often the case, say in solvent naphtha, substances with similar colour-reactions, such as trinitro-pseudocumene, 2, 4-di- und 2, 4, 6-trinitro-toluene must be previously removed. This will be an easy task if we avail the small solubility of triniro-*m*- and -*p*-xylenes in ordinary solvents, such as ether, alcohol, and acetone.

II. Microscopic Method.

An application of a polarisation microscope for identification of a very minute quantity of substances has already been recommended by Emich,(2) Behrens,(3) and others. In case of mixture, however, it is applicable only under the following conditions: (1) Crystals to be examined should be of different optical properties. (2) Crystals of each component should be roughly separated by some suitable solvents. This condition is necessary to raise accuracy and sensitivity of the result.

Besides, when refractive indices of a crystalline organic compound are measured by immersion-method, it must be kept in mind that organic substances, different from inorganic ones, are more or less soluble in immersion-media. And as this always causes the change of refractive indices of the media, we can not often find the true values for refractive indices of organic substances. For analytical purpose, however, accurate values for refractive indices are not necessary, and it is sufficient to find a medium which stands, with regard to refractivity, in different relations with each component of the mixture in question.

(1) Actual treatments shall be described in a later paper.

(2) Emich, "Lehrbuch der Mikrochemie", 2 Aufl. (1926), 21.

(3) Behrens-Kley, "Mikrochemische Analyse", I, 4 Aufl. (1921); "Organische Mikrochemische Analyse", 2 Aufl. (1922).

Now, to detect the three isomers of xylene under microscope, we must first obtain their crystalline derivatives. As a simple and effective method for this purpose, so-called "direct substitution" processes, nitration, bromination, and sulphonation, were tried.

1. **Esotetrabromo-compounds.** Among various brominated xylenes, esotetrabromo-xylenes are the most preferrable for its easiness of formation and for having no isomers. Properties important for distinction of the three esotetrabromo-xylenes are given in Table 1.

TABLE 1.

	Esotetrabromo-*o*-xylene.	Esotetrabromo-*m*-xylene.	Esotetrabromo-*p*-xylene.
Melting point.	258°*	240°**	253°
Solubility.	Soluble in hot $CHCl_3$; sparingly in cold.	Soluble in cold $CHCl_3$; soluble in hot acetone.	A little soluble in cold $CHCl_3$; sparingly in hot acetone.
Properties of crystals.	White silky needles; extinction straight; elongation negative.	The same.	The same.
For Aniline.	$n_1 > N$.***	n_1 slightly $> N$.	$n_1 > N$.
For α-Br-$C_{10}H_7$ and CH_2I_2.	A little soluble.	Readily soluble.	Readily soluble.
	$n_2 \gtrsim 1.8$.****	The same.	The same.

* Values reported by different observers are not same: 261° (Klages and Sommer), 254–5° (Blümlein), 260° (Jacobsen).

** 240° (Fittig and Bieber), 247° (Auwers and Krieckritz).

*** n_1 and n_2 are indices of the faster and the slower rays in a crystal respectively. Therefore, always $n_1 < n_2$. In this report N represents refractive index of the medium in question, but is not always equal to that of the pure medium.

**** As the consequence of having 4 atoms of Br in one molecule, these compounds have such extremely high refractive indices, that n_2 cannot be measured with ordinary immersion-media. This is a drawback of these compounds.

Though we have solvents to separate the three tetrabromo-compounds, their optical properties, as shown in the table, are insufficient to distinguish them. In short, they are not proper derivatives to identify three isomeric xylenes under microscope.

2. **Trinitro-compounds.** *o*-Xylene is difficulty nitrated, trinitro-*p*-xylene can not have any isomer structurally. Only *m*-xylene is capable to form three isomeric trinitro-derivatives, but as the consequence of the orienting influence of the two meta-standing methyl- and of added nitro-groups, 2, 4, 6-trinitro-*m*-xylene is the only product obtained by the direct substitution with nitrating acid. Here again, the trinitro-compounds are rather easily prepared than the lower ones. Some properties of trinitro-*m*- and -*p*-xylenes are shown in Table 2.

TABLE 2.

	2,4,6-Trinitro-*m*-xylene.	2,3,5-Trinitro-*p*-xylene.
Melting point.	179°*	137–8°
Solubility.	Very sparingly soluble in alcohol and acetone, both in hot and cold.	Very sparingly soluble in hot and cold alcohol; soluble in hot acetone.
Crystalline form, etc.,	Thin prisms or hexagonal plates, with beautiful interference colour; pale yellow.	Thick prisms; light yellow.
Optical properties.	Extinction straight; elongation positive.**	Extinction straight;*** elongation negative.
For α-Br-$C_{10}H_7$.	$n_1 < N < n_2$ (for prisms); $n_2 \cdot N$ (for plates).	$n_1 > N$.

* Here again, values given by different observers are not concordant 176° (Grevingk), 177° (Luhmann), 180–1° (Knoevenagel), 182° (Tilden).

** Freshly formed crystals have elongations both positive and negative, but crystals recrystallised from alcohol have only positive elongation.

*** Trinitro-*p*-xylene crystallises in monoclinic prisms, but the cleavage being perfect toward (001), the face most frequently observed is (001) [Groth, "Chemische Krystallographie," IV, 667]. Hence nearly all crystals extinct in straight position. Very few crystals show oblique extinction. Their angle of extinction amounts about 30° [28° (Groth)].

As it is evident from the above table, the trinitro-compounds are most satisfactory derivatives for the identification of *m*- and *p*-xylenes.(1) Their refractive indices need not be measured. We are only to determine their signs of elongation. However, it is better to make sure of the result by determining the refractive indices.

3. Sodium salts of the sulphonic acids. Trinitro-derivatives leave little to be desired for the detection of *m*- and *p*-xylenes. But as we have not a suitable method to detect *o*-xylene, finally sulpho-derivatives were examined.

o-Xylene easily forms 4-sulphonic acid when treated with conc. sulphuric acid at 80–90°C.(2) Under the same condition *m*-xylene forms 4- and 2-sulphonic acids, but the former in far larger quantity.(2) *p*-Xylene-sulphonic acid is usually obtained by dissolving *p*-xylene in weak fuming sulphuric acid,(2) and one of the technical methods to separate *p*-xylene is based on its insolubleness in ordinary conc. sulphuric acid. However, I have observed that under the above condition, it is also easily converted into 2-sulphonic acid, as Crafts(3) has already mentioned.

(1) A sample, very rich in *m*- or *p*-xylene, can be determined simply from the observation of its nitration. When a sample is very rich in *p*-xylene, dinitro-*p*-xylenes separate out as a crystalline mass, during or after the addition of nitrating acid. In the case of a sample containing a large quantity of *m*-xylene, trinitro-*m*-xylene crystallises out in beautiful long needles from the reacting mixture, when heated in an oil bath.

(2) Jacobsen, *Ber.*, **10** (1877), 1009; **11** (1878), 22.

(3) *Z. anal. Chem.*, **32** (1893), 243.

For the purpose of identification under microscope, their barium salts were first compared. Solubility in water markedly decreases in the order of *m*-, *o*-, and *p*-derivatives, but they proved unsuitable for analytical purpose, for *o*- and *m*-compounds only form crystalline crusts, without giving well-defined crystals.

The sodium salts were next prepared from the barium salts, and their properties compared (see Table 3).

TABLE 3.

	Na *o*-xylene-4-sulphonate.	Na *m*-xylene-4-sulphonate.	Na *p*-xylene-2-sulphonate.
Solubility.	Not readily soluble in H_2O; soluble in hot alcohol, not readily in cold.	Soluble in H_2O; soluble in alcohol.	Not readily soluble in H_2O; a little soluble in hot alcohol; sparingly in cold.
Crystalline form.	Prisms or flat needles.	Well-defined rhombic plates.	Prisms or flat needles.
Optical properties.	Extinction straight; elongation positive.	The same.	The same.
For cedar oil	$n_1 < N$.	$n_1 \geqq N$.	$n_1 > N$.
For $C_2H_4Br_2$	$n_1 < N < n_2$.	$n_1 < N < n_2$.	$N < n_1 < n_2$.

The crystals of sodium sulphonate of *p*-xylene are distinguished from its isomers by its refractive indices. But the *o*- and *m*-compounds cannot be distinguished by this way, the only key in this case being their crystalline forms. The *m*-compound when slowly crystallises out from alcohol, forms well-defined rhombic plates, the two internal angles of which are about 80° and 100° respectively, while the *o*-compound crystallises in prisms or in flat needles. Consequently *o*-compound is detected by finding prismatic crystals whose smaller refractive index is lower than that of cedar oil.

It must be here added, however, that, as the crystalline forms of the salts of these sulphonic acids seem to have tendency to be easily disturbed by the presence of their isomers, we cannot expect the results of this method to be highly sensitive.

An Actual Example.

All the above mentioned methods were tested with various mixtures and proved to be applicable. An example of the analysis of commercial xylene shall be briefly described.

"Xylol" on market was distilled with Hempel's still-head, and two fractions, 135–8°C. and 140–2°C. were taken.

Detection of *m*- and *p*-xylenes. To 1 c.c. of the first fraction, 10 c.c. of the nitrating acid[1] (conc. H_2SO_4 1 : fuming HNO_3 2) were slowly added under water tap. The mixture was then heated in an oil bath at 110–120°C. for an hour, and the content was poured into water. The raw product was purified by washing with ether, and by recrystallising from a large amount of alcohol. Then the detection of isomeric xylenes in the sample was carried out in two ways.

By colour-reaction. When one portion of crystals thus obtained was tested in alcoholic solution with KOH, the intense green coloration instantly occurred. (Presence of *m*-xylene!) Next, the other portion was treated with hot acetone, when the greater part remained undissolved. (This shows that the sample was very rich in *m*-xylene.) The acetone solution gave the red coloration with KOH. (Presence of *p*-xylene!)

By microscopic method. Crystals, which remained undissolved in hot acetone, were examined under microscope; they had straight extinction and positive elongation, and their refractive indices stood in the following relation: $n_1 < \alpha$-bromonaphthalene $< n_2$. These crystals are nothing but trinitro-*m*-xylene. On the other hand, those separating out from acetone solution on cooling were found to be a mixture of two crystals, one of which was of positive elongation and the other negative, and the mixture contained the latter in far larger quantity. Those crystals with positive elongation proved to be trinitro-*m*-xylene from their refractive indices, and those of negative elongation were ascertained to be trinitro-*p*-xylene, for both of their refractive indices were greater than that of α-bromonaphthalene.

Detection of *o*-xylene. When 1 c.c. of the second fraction was shaken with equal volume of conc. H_2SO_4 at 80–90°C. for 30 minutes, nearly all the sample was absorbed in the acid. The sulphonic acids were converted into Ba salts in usual way, and from their aqueous solution two fractions of crystals were obtained. Dissolving each fraction in hot water, Ba was precipitated with a_2NCO_3. The filtrate was evaporated to dryness, and the sodium sulphonates were extracted with hot alcohol.[2] Crystals separating out from the somewhat concentrated alcoholic solution were not well-defined, and found in an aggregate state. Few prismatic crystals were found, but they proved to be the *p*-compound by their refractive indices. None of the crystals had properties of the *o*-compound, thus proving its absence.

To make sure, another c.c. of the second fraction was brominated with an excess of bromine in the presence of reduced iron. The product after

(1) An excess of nitrating acid must be added, otherwise, *p*-xylene forms only dinitro-derivatives which are readily soluble in ether.

(2) Sodium sulphonates were also prepared directly by dropping the mixture of the raw sulphonic acids with excess of conc. H_2SO_4, in 4 times its volume of saturated NaCl solution.

washing with alkali and HCl successively, was several times recrystallised from chloroform, collecting every time crystals separating out first. Long white needles finally obtained melted at 252–3°C., which is exactly the m. p. of the pure esotetrabromo-*p*-xylene.

Thus in the commercial xylene in question no appreciable quantity of *o*-xylene was detected.

Appendix.

As the above mentioned principle,[1] on which one of the technical methods of separating *p*-xylene from its isomers is based, seems to be very doubtful, I have re-examined the method.

Five hundred c.c. of the commercial xylene, same as that used in the above experiments, was shaken with equal volume of conc. H_2SO_4 for 30 min., and the unabsorbed portion, which was only few percent of the sample, was fractionated. The first drop distilled at 145°C., and the thermometer rapidly rose to 160°C., while the b. p. of *p*-xylene is 135–6°C. Here, we can conclude that nearly all *p*-xylene was absorbed in sulphuric acid, consequently this technical method is not recommendable for that purpose.

Summary.

Methods to detect and identify the three isomeric xylenes in their mixture, especially in limited quantity, are given.

1. *m*-Xylene and *p*-xylene, even in minute quantity, can be successfully identified as their trinitro-derivatives, by their colour-reactions in alcoholic or acetone solution toward alkali, or by the optical properties of their crystals. These two methods leave little to be desired.

2. *o*-Xylene is identified microscopically as sodium sulphonate, but in case of a mixture very poor in *o*-xylene, we can not expect a result of high sensitivity by this method.

3. The technical method to separate *p*-xylene from its isomers, based on its insolubility in ordinary conc. sulphuric acid, is tested and shown to be of little value.

In conclusion, I must express my hearty thanks to Dr. I. Okada for his kind help in practical treatment of the microscope.

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(1) See p.196.

STUDIES ON THE BROMINATION OF TETRA-ETHYL DICARBOXY-GLUTACONATE AND REMARKS ON THE CONSTITUTION OF THE GLUTACONIC ACIDS.

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In the last two years the author published some papers dealing with studies on the derivatives of glutaconic acid.[1] The first experiment was the bromination of tetraethyl dicarboxyglutaconate, the object of which was, in the first place, to obtain tetraethyl α, β-dibromodicarboxyglutarate; and this theme was given by Prof. K. Matsubara. Since the expected result was not obtained, it was given up without further investigations, and another compound with a similar constitution, diethyl dicyanoglutaconate, was taken as the substance to be subjected to the action of bromine. What the so-called diethyl dicyanoglutaconate is, and how it is acted on by bromine, were already described in details.[2] In the meantime it seemed that some important results might be brought out by tracing the reaction between bromine and tetraethyl dicarboxyglutaconate. Experiments have been newly repeated, with the results described in the following pages.

Action of Bromine on Tetraethyl Dicarboxyglutaconate. When bromine was added to the ester in the proportion of 2 Br : $C_{15}H_{22}C_8$, and the mixture was well stirred, the colour of bromine almost disappeared after a moment and hydrogen bromide was generated at the same time. The reaction mass was diluted with ether, shaken with aqueous alkali, washed with water, dried, and evaporated in vacuo. An oily substance remained; but hydrogen bromide was again genarated.

The elimination of hydrogen bromide was completed through the following treatment. An ethereal solution of pyridine in an amount equimolecular to the ester was added to such of the reaction product of bromine and tetraethyl dicarboxyglutaconate. After standing for a night the ethereal solution was freed from pyridine hydrobromide by washing it with water, and further it was washed successively with dilute sulphuric acid, dilute alkali, and water. The solution was dehydrated and evaporated in vacuo over concentrated sulphuric acid, when a colourless oil was obtained which splitted off hydrogen bromide no more. 0.1858 And 0.1780 gr. of the substance gave respectively 0.0876 and 0.0843 gr. of AgBr. (Found : Br = 20.06 ; 20.15. $C_{15}H_{21}O_8Br$ requires Br = 19.54.%) In one experiment 29.8 gr. of the product was obtained from 24.2 gr. of $C_{15}H_{22}O_8$ and 11.7 gr. of bromine,

(1) This journal, **2** (1927), 26; 236; 278; 305; **3** (1928), 102.
(2) This journal, **2** (1927), 26.

the theoretical yield calculated from the following equations being 30 gr. It is shown by these numbers that the product was formed according to the following equations:

$$C_{15}H_{22}O_8 + 2\,Br = C_{15}H_{22}O_8Br_2,$$
$$C_{15}H_{22}O_8Br_2 = C_{15}H_{21}O_8Br + HBr,$$
$$HBr + C_5H_5N = C_5H_5N.HBr.$$

The reaction resulted as if a substitution took place, but really it consisted of two processes of addition of 2 Br and elimination of HBr, because the calculated amount of bromine was consumed at once, and the elimination of hydrogen bromide was not complete unless the product was treatad with pyridine.

The intermediate product formed by addition of 2 Br to $C_{15}H_{22}O_8$, has, of course, the formula $C_{15}H_{22}O_8Br_2$ and the following constitution:

$$(C_2H_5OCO)_2CBr-CHBr-CH(COOC_2H_5)_2.$$

This addition product splits off a molecule of hydrogen bromide, and this dissociation is complete in the presence of pyridine which fixes the hydrogen bromide.

Hydrogen bromide may possibly be splitted in three ways, and the produced bromo-ester may have one of the following formulae:

(I) $(C_2H_5OCO)_2CBr-CH = C(COOC_2H_5)_2$,

(II) $(C_2H_5OCO)_2C = CBr-CH(COOC_2H_5)_2$,

(III) $(C_2H_5OCO)_2C-CHBr-C(COOC_2H_5)_2$.

It is impossible for such a three-carbon ring as shown by formula (III) to be formed by elimination of hydrogen bromide, and this formula is excluded, if the result of saponification of the bromo-ester is further taken into account. The bromo-ester possesses no acid hydrogen, for it does not dissolve in alkali, and formula (II) is also improbable. The following experiment settles the question, indicating that the bromo-ester is most reasonably represented by formula (I).

When bromine was added to tetraethyl α-methyldicarboxyglutaconate $(C_2H_5OCO)_2C(CH_3)-CH=C(COOC_2H_5)_2$, in which the acid hydrogen is replaced by a methyl group, a part of bromine combined with the ester after a short time, the colour fading to some extent, but never completely even if the bromine was used in an amount much smaller than two atoms to one molecule of the ester, while the elimination of hydrogen bromide was not detected. This observation ascertained the existence of equilibrium in the following reversible reaction:

$$C_{16}H_{24}O_8 + 2\,Br \rightleftarrows C_{16}H_{24}O_8Br_2$$

In the ethereal solution this reaction is fixed. Thus, when the reaction mixture was dissolved in ether, shaken with an aqueous solution of sodium sulphite, washed with water, dried and evaporated in vacuo, the remaining

see errata, V. 3, P. 321

colourless oil soon spitted bromine and became red. The addition of bromine to tetraethyl dicarboxyglutaconate is nearly complete, causing the elimination of hydrogen bromide, and that to a limited extent, while the action of bromine on tetraethyl α-methyldicarboxyglutaconate can proceed only incompletely, the elimination of hydrogen bromide being impossible here. In both cases the saturated compounds formed by the addition of bromine is in equilibrium with unsaturated compounds, in the former case the unsaturated bromo-ester $C_{15}H_{21}O_8Br$ being produced by a secondary change of the saturated addition product, while in the latter a part of the original uusaturated ester being left intact. This difference must be attributed to the presence of the acid hydrogen in the one, and the absence in the other. In other words, when hydrogen bromide is splitted from the saturated dibromo-ester, the acid hydrogen takes part in the formation of hydrogen bromide. Therefore, the unsaturated bromo-ester $C_{15}H_{21}C_8Br$ misses the acid hydrogen and must be the compound represented by fomula (I) which should be called tetraethyl α-bromodicarboxyglutaconate. The bromine atom remaining in the bromo-ester is situated in the γ-position of the original ester, tetraethyl dicarboxyglutaconate, but it may be designated as the α-substituent in comformity to the subsequent arrangement of the propylene nucleus, in which the single and the double bonds exchange their positions during the addition of bromine and elimination of hydrogen bromide.

see errata V. 3, P. 321

A substance with the same composition and constitution as the above bromo-ester has been already known and obtained by the interaction of bromine and the sodium or cupric derivative of tetraethyl dicarboxyglutaconate.(1) Recently F. Faltis and J. Pirsch(2) obtained tetraethyl allene-tetracarboxylate by the action of silver oxide on this bromo-ester.

Hydrolysis of Tetraethyl α-Bromo-dicarboxyglutaconate. The bromo-ester, formed by the elimination of hydrogen bromide from the addition product of bromine to tetraethyl dicarboxyglutaconate, was hydrolysed by boiling with hydrochloric acid. The product was obtained in various grade of purities according to the conditions of saponification. It has been found that a large quantity of alcohol must be present in order to get the product in a state free from resinous coloured contamination, the presence of alcohol accelerating the reaction at the same time. The following proportion gave a good result. The mixture of the bromo-ester 25 gr., alcohol 70 gr., concentrated hydrochloric acid 100 gr., and water 30 gr, is boiled for 3 or 4 hours with a reflux condenser, and the solution is evaporated on the water bath. When the solution is evaporated to a small volume, a further amount of

(1) Guthzeit and Hartmann, *J. prakt. Chem.*, [2] **81** (1910), 350; F. Faltis and Carla Ruiz de Roxas, *Monatsh.*, **42** (1922), 459.

(2) *Ber.*, **60** (1927), 1621.

concentrated hydrochloric acid is added, the solution is evaporated to dryness, and the crystalline mass is dehydrated in a desiccator over concentrated sulphuric acid and soda-lime. In one experiment 24.6 gr. of the bromo-ester gave 9.3 gr. of the crude product in brownish crystals. If the saponification proceeded according to the equation :

$$(C_2H_5OCO)_2CBr-CH=C(COOC_2H_5)_2 + 4\,H_2O$$
$$HOOC-CHBr-CH=CH-COOH + 4\,C_2H_5OH + 2\,CO_2,$$

the above quantity of the bromo-ester must yield 12.6 gr. of the product. This result suggested some unexpected change. In fact it was found that the saponification product was no longer a compound of bromine, but it contained chlorine. This crystalline compound was purified by repeated recrystallization from a little amount of water until it showed a nearly constant melting point 155°. In order to make the recrystallization most effective, it was necessary to remove entirely the mother liquor each time. The mother liquor was well drained off by sucking the crystals in a Gooch crucible with a filter paper fitted at the bottom, and pouring pure benzene on the crystals, the sucking being continued. After the last recrystallization the crystals were well dried over sulphuric acid. It is colourless, easily soluble in water, alcohol, acetic acid, acetone, and ether, but difficultly soluble in benzene and chloroform. It is readily oxidized by the alkaline permanganate solution and is found to be an unsaturated acid. 0,3498 Gr. of the substance gave 0.4662 gr. of CO_2 and 0.0954 gr. of H_2O; 0.2134 gr. of the substance gave 0.2840 gr. of CO_2 and 0.0574 gr. of H_2O; 0.2374 gr. of the substance gave 0.2042 gr. of AgCl. (Found : C=36.36, 36.31; H= 3.05, 3.01; Cl=21.28. $C_5H_5O_4Cl$ requires C=36.47; H=3.06; Cl=21.56%.) It is doubtlessly a chloroglutaconic acid.

Hitherto only one chloroglutaconic acid has been known, and that is β-chloroglutaconic acid melting at 129°[1]. Now another chloroglutaconic acid melting at 155° has been obtained. These two kinds of acids are subjected to the similar treatment at the last process of preparation, that is, saponification with hydrochloric acid, and it is supposed that they are not geometrical isomers to each other. Hence the chloroglutaconic acid, the constitution of which is now under discussion, must be one of the following isomers :

(IV) α-chloroglutaconic acid, $HOOC-CHCl-CH=CH-COOH$;
(V) γ-chloroglutaconic acid, $HOOC-CH_2-CH=CCl-COOH$.

Now it must be considered how the bromine atom in the bromo-ester $C_{15}H_{21}O_8Br$ is replaced by a chlorine atom during its saponification giving the chloroglutaconic acid. This is well understood if it is supposed that the

(1) Burton, Pechmann, *Ber.*, 20 (1907), 147 ; Inyold Nickolis, *J. Chem. Soc.*, 121 (1922), 1638.

addition of hydrogen chloride and at the same time the elimination of hydrogen bromide take place. It is natural to consider that, if addition is easy to take place, then the inverse reaction may be also easily realised. Thus if the compound with bromine is less stable than that with chlorine in the saponifying medium where the concentration of hydrogen chloride is much greater than that of hydrogen bromide even after the replacement of the halogens has been finished, it is not surprising that the addition of hydrogen chloride and the elimination of hydrogen bromide take place simultaneously.

In whatever manner addition and elimination may take place, a compound of the type (V) can not be formed. Hence the chloroglutaconic acid in question must have formula (IV). Now, after the constitntion of the saponification product has been determined in this way, the mechanism of the formation of the chloro-acid from the bromo-ester can be explained to some extent as follows:

$$\rangle CBr-CH=C\langle \xrightarrow{+HCl} \rangle CBr-CH_2-CCl\langle \xrightarrow{-HBr} \rangle C=CH-CCl\langle$$

It is probable that hydrogen chloride adds in such a manner that enables the chlorine atom to take the position the most remote from the bromine atom. The above reaction may occur probably in every stage of the saponification.

The tetraethyl α-bromodicarboxyglutaconate prepared by Faltis' method was saponified by the same procedure, and the product was recrystallised from water several times. 0.2024 Gr. of the substance gave 0.2708 gr. of CO_2 and 0.0556 gr. of H_2O; 0.2064 gr. of the substance gave 0.1724 gr. of AgCl. (Found: C=36.50; H=3.07; Cl=20.66. $C_5H_5O_4Cl$ requires C=36.47;, H=3.06; Cl=21.56%.) The quantity of the substance was too small to be purified to a constant melting point, but the substance melted at 154°, and the mixture of this specimen and the α-chloroglutaconic acid described in the preceding pages melted at 154°, which showed the identity of the two specimens.

By the studies described in this paper it has been found that in the derivative of glutaconic acid addition and simultaneous elimination can easily take place, and the most stable compound in the condition is obtained as the final product, without destroying the structure of the propylene chain. If the substance which adds to a glutaconic derivative is the same as that is eliminated from the intermediate saturated compound, this transformation will not be detected by analysis of the final product; but it is possible that the final product differs from the substance not yet subjected to this transformation; in other words, the movement of the double union is possible. For instance, if a glutaconic

derivative containing no halogen is hydrolysed with hydrochloric acid, hydrogen chloride may add to the unsaturated bond in such a manner that hydrogen will take the γ-position, chlorine the β-position, according to the usual rule of addition to an unsaturated acid, and then the chlorine may be splitted with α-hydrogen in the following manner:

$$HOOC\cdot CR:CR'\cdot CHR''\cdot COOH + HCl \rightarrow HOOC\cdot CHR\cdot CR'Cl\cdot CHR''\cdot COOH$$
$$\rightarrow HOOC\cdot CHR\cdot CR':CR''\cdot COOH + HCl.$$

This must be borne in mind when one carries out an experiment such as the saponification of the derivatives of glutaconic acid by means of hydrochloric acid. It is not meant that such a transformation can take place only in the derivatives of glutaconic acid, but that it is possible at least in this class of organic compounds. In one experiment of saponifying the bromo-ester, hydrochloric acid was replaced by sulphuric acid. and the product was examined. After removing the sulphuric acid by adding the calculated amount of barium carbonate, the solution was filtered from barium sulphate and evaporated on the water bath. On concentrating it the white fume of hydrogen bromide was evolved. The product, after recrystallisation from water, was found to contain nearly no halogen. Thus, in the saponification with sulphuric acid the reaction is also so complicated that the constitution of the product can be difficultly deduced from that of the starting substance.

This consideration may bring an important consequence upon the theory which has been held on the constitution of the glutacodic acids by certain investigators who have been working in this interesting field of organic chemistry.

Remarks on the Constitution of the Glutaconic Acids. In 1905 J. F. Thorpe[1] found that the α- and γ-positions in the glutaconic acids are the same, for instance, α, β-dimethylglutaconic acid $HOOC-CH(CH_3)-C(CH_3)=CH-COOH$, and β, γ-dimethylglutaconic acid, $HOOC-CH_2-C(CH_3)=C(CH_3)-COOH$, are identical. From this fact he gave the glutaconic acid and its derivatives the symmetrical formula, the so-called normal form, and the constitution of glutaconic acid was represented by the formula $HOOC-CH-CH_2-CH-COOH$. Since then he and his collaborators have been making many important investigations in this sphere, among which some indicated also the identity of the α- and γ-positions in the glutaconic acids.[2] Feist[3] rejected Thorpe's theory of the normal form, and has been supporting the ordinary formula until the present. Feist held the theory of oscillation in order to explain the existence of only one form of glutaconic acid and the

(1) *J. Chem. Soc.*, **87** (1905). 1669.
(2) *J. Chem. Soc.*, **89** (1906), 631; **99** (1911), 2187.
(3) *Ann.*, **345** (1906), 117; **370** (1909), 41; **428** (1922), 25.

identity of the α- and γ-positions of this acid, and he has been also making many important studies on the derivatives of this acid. Not only Feist, but also any other chemists, have not suspected the uncertainty involved in the experiments showing the identity of the α- and γ-positions of glutaconic acid, on which the standpoint of Thorpe's theory of the normal form was based. In all of the experiments which were taken as the proofs of the identity of the α- and γ-positions the substituted glutaconic acids were obtained by the saponification process with concentrated hydrochloric acid. Now, the present author has shown that the constitution (the position of the double union) of the product can not be deduced from that of the starting substance in a reaction such as the saponification of the glutaconic derivatives with hydrochloric acid. Thus the imperfection in Thorpe's conclusion is pointed out. If the experiments resulted as if the α- and γ-positions were the same, it must be rather concluded that the migration of the double union took place during the reaction. He recognised the migration of the double union when he dealt with the action of sodium ethylate on the derivatives of the glutaconic ester, and even a rule of migration of the double union was devised.[1] It is unnatural to assume the fixity of the double union in the saponification with hydrochloric acid and to conclude the identity of the α- and γ-positions.

A hypothesis as Thorpe's seems to be no longer necessary in the chemistry of the glutaconic acids, and, therefore, the present author will support the opinion held by Feist, but it seems that his theory of oscillation is also no longer indispensable, for it is now the fact of existence of only one form of glutaconic acid that this theory is to explain, and this fact can be easily understood if it is supposed that only one form is stable.

In the paper on the nitrile-esters of the dicarboxyglutaconic acid,[2] the mechanism of the condensation of an ethoxymethylene compound $C_2H_5OCH=CXY$ with a sodio-methylene compound $CHNaX'Y'$ was explained on the assumption that the theory of the normal form can be applied to the derivatives of dicarboxyglutaconic acid. This explanation must be corrected according to the results of the recent investigations which showed that Thorpe's theory of the normal form had been based on somewhat uncertain evidences. In this paper it is stated only that the explanation must be corrected, and how the mechanism of the above condensation is correctly explained will be published in another paper, for it is necessary further to carry out such experiments as will throw light on the consideration of the reactions of this kind.

(1) *J. Chem. Soc.*, **101** (1912), 249.
(2) This journal, **2** (1927), 282.

Summary.

By the action of bromine on tetraethyl dicarboxyglutaconate, tetraethyl α-bromodicarboxyglutaconate was obtained as the final product. When the tetraethyl α-bromodicarboxyglutaconate was saponified by means of hydrochloric acid, the product was α-chloroglutaconic acid. According to the result of this investigation, it was concluded that, when one carries out the saponification of a derivative of glutaconic acid, the constitution of the product cannot be deduced from the starting substance. Uncertainty in J. F. Thorpe's theory of the normal form was pointed out.

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